

**Studies on Syntheses and Permeabilities
of Special Polymer Membranes**
**34. Permeation Behavior of Glycerol Aqueous Solution
Through Cellulose Ester Membranes**

Tadashi Uragami, Yasuhiro Sugitani and Mizuho Sugihara

Department of Chemistry, Faculty of Engineering, Kansai University,
Osaka, 564, Japan

Summary

The permeabilities of various cellulose ester membranes and cellulose membranes were investigated using pure water and aqueous solution of glycerol as feed. In all membranes, the permeation rate for aqueous solution of glycerol was greater than for pure water. The permeation rates of cellulose ester membranes increased with an increase in number of carbon atoms of the substituent group in cellulose ester.

Introduction

In earlier papers, it has been reported that the permeation rate for aqueous solution containing a hydrophilic solute through hydrophilic polymer membranes such as membranes of crosslinked poly(vinyl alcohol)¹, interpolymer² prepared from poly(vinylidene fluoride) and poly(styrene sulfonic acid), and cellulose³ was greater than for pure water. This permeation behavior was explained by the following three factors: (a) the size of water cluster, (b) activation of water molecules attaching to bound water on the membrane surface and in the membrane, (c) plasticization of polymer membrane material. In the present paper the membranes were prepared from various cellulose esters in order to neglect the factors of (b) and (c); the permeation behavior through these cellulose ester membranes is discussed by comparing with that of cellulose membrane.

Experimental

Materials Cellulose powder (Cell)(produced by Sanyo Kokusaku Pulp Co. Ltd., W-4) which was dried under reduced pressure was employed as membrane substance. Pure commercial 1,4-dioxane was as solvent for the casting solutions of cellulose ester membranes. Reagents used for preparation of cellulose membranes and for syntheses of cellulose ester derivatives were pure commercial sources. Pure commercial glycerol was used as feed solute.

Syntheses of cellulose ester derivatives Cellulose powder (16.2 g) was dispersed in 1,4-dioxane (344.3 ml) in a three-necked flask fitted with a sealed stirrer, 4.5 times of pyridine per unit mole of glucose was added, and then this mixture was stirred for 30 min at 85 °C. Subsequently, 1,4-dioxane solution, same volume as volume of acid chloride, which contained 2 to 9 moles of corresponding acid chloride per unit mole of glucose was added to the above mixture and these mixtures were stirred for 48 h at 85 °C, then were allowed to stand for several hours at room temperature. The reaction mixtures were poured into distilled water with good agitation. Solid products were filtered off by the glass filter repeatedly with distilled water until the filtrates become colorless clear solutions, and washed throughly with methyl alcohol. Cellulose esters were dried under reduced pressure at 65 °C, dissolved in 1,4-dioxane, and reprecipitated with methyl alcohol containing a small amount of water. In order to remove 1,4-dioxane, pyridine, and organic acids in the ester polymers the above procedure was repeated and white products were obtained.

Preparation of membranes Cellulose membranes were made by the method described in an earlier paper³. The casting solutions were prepared from systems of cellulose ester (2 g)/1,4-dioxane (80 g). Cellulose ester derivative membranes were made by poring these casting

solutions onto a rimmed glass plate, allowing to evaporate the solvent at 50 °C for 20 min.

Results and Discussion

The infrared absorption spectra of cellulose ester derivatives are shown in Figure 1. In the spectra of

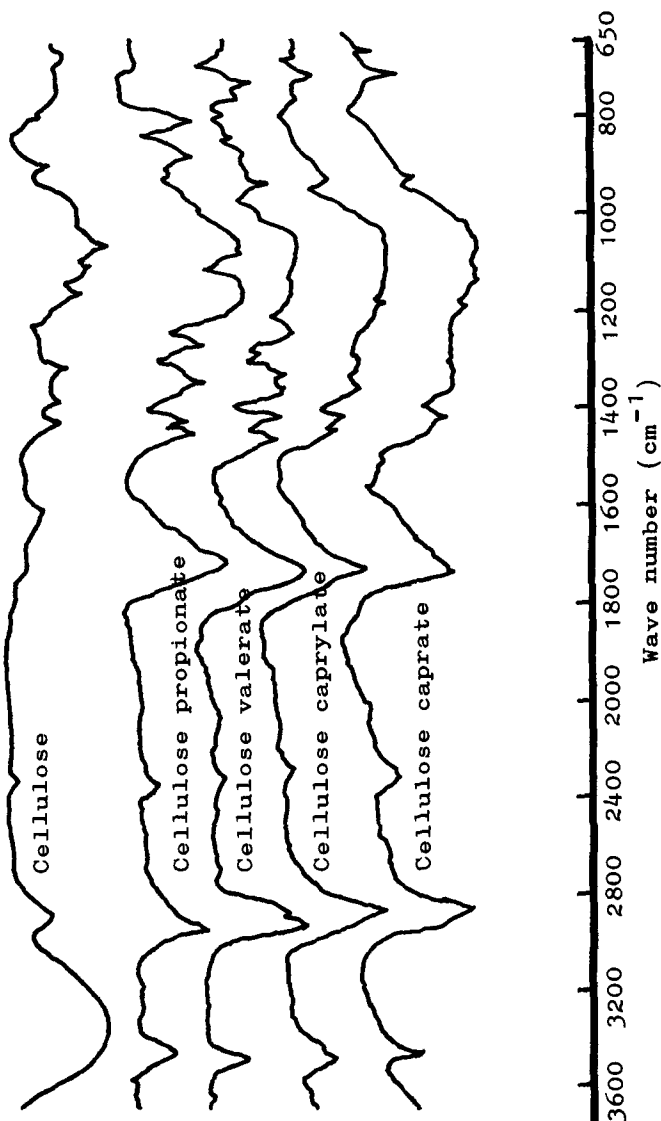


Figure 1 Infrared spectra of cellulose and cellulose ester derivatives.

cellulose esters the absorption bands of the O-H stretching vibration at 3400 cm^{-1} decrease, the bands of the $-\text{CH}_2-$ stretching vibration at 2900 cm^{-1} increase, the characteristics absorption bands of the C=O stretching vibration at 1750 cm^{-1} significantly appear, the absorption bands at $1050-1300\text{ cm}^{-1}$ are due to the $-\text{C}-\text{O}$ stretching vibration in the ester bond, and the absorption peaks at 700 cm^{-1} are assigned to the skeletal vibration of $(\text{CH}_2)_n$. It is seen from these spectra that the corresponding cellulose esters are synthesized. Table 1 summarizes the degree of substitution, which are calculated from the values of elemental analysis, and the yields of cellulose ester derivatives.

Figure 2 shows the permeabilities of cellulose membrane and various cellulose ester membranes, using pure water and aqueous solution of glycerol as feed solution. The permeation rate of cellulose propionate membrane is smaller than that of cellulose membrane. This result may be attributed to the fact that the dissolution of water molecules into cellulose propionate membrane is more difficult and the size of water cluster increases because of an increase of hydrophobicity of the membrane. When the number of carbon

Table 1
Analytical results of cellulose ester derivatives

Product	Degree of substitution	Yield (%)
Cellulose propionate	2.5	94
Cellulose valerate	2.7	88
Cellulose caprylate	2.4	94
Cellulose caprate	2.4	92

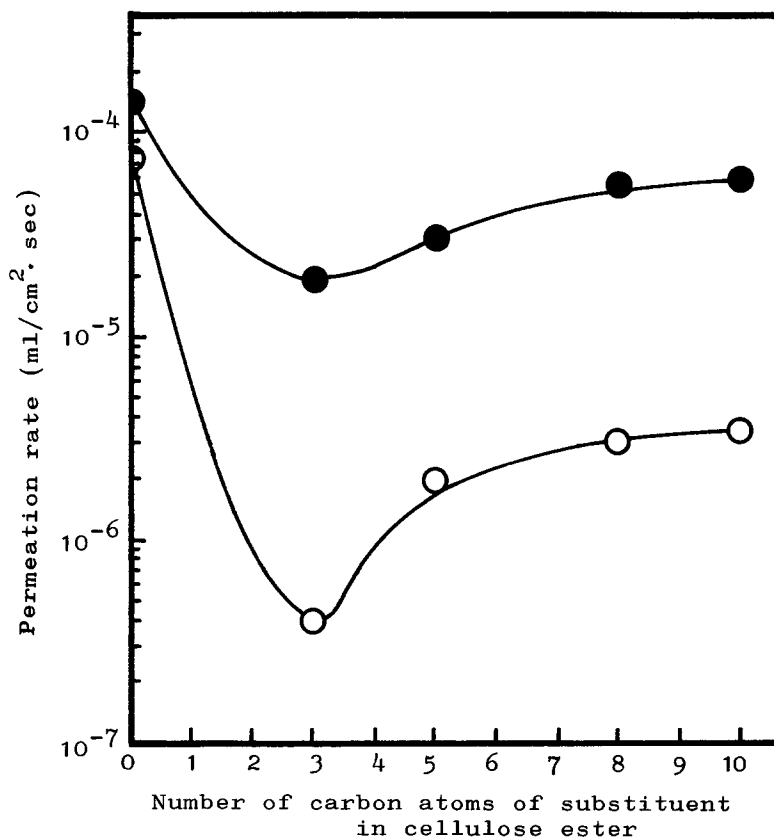


Figure 2 Permeabilities of cellulose and cellulose ester membranes. Feed: (○) pure water, (●) aqueous solution of glycerol ($1.1 \times 10^{-2} \text{M}$) ; operating conditions: 40°C , 4kg/cm^2 .

atoms of substituent in cellulose ester increases, the permeation rate becomes larger. This phenomenon is due to a decrease of crystallinity of the membrane because the substituent groups in cellulose ester derivatives act as the species of internal plasticization.

On the other hand, the permeation rate for aqueous solution of glycerol is greater than for pure water. Furthermore, the difference between these permeation

rates for pure water and aqueous solution of glycerol through cellulose ester membranes is more remarkable than the difference of permeation rate through cellulose membrane. In cellulose ester membranes having more large water cluster, it is presumed that the addition of glycerol acts significantly the rupture of water cluster. Therefore, the permeation rate for aqueous solution of glycerol may be increased.

The amounts of bound water determined by differential scanning calorimetry are zero for all cellulose ester membranes. This is due to very small interaction between the cellulose ester membranes and the water molecules because of very strong repulsion between the hydrophobic groups and the water molecules. Consequently, it is implied that the permeation of pure water through these cellulose ester membranes follows the capillary flow.

References

- 1 T. Uragami, T. Furukawa, M. Sugihara, Tech. Rept. Kansai Univ., 22, (1981) 99
- 2 T. Uragami, M. Fujimoto, M. Sugihara, Desalination, in press
- 3 T. Uragami, Y. Sugitani, M. Sugihara, Polymer, submitted for publication

Received January 5, 1981

Revised February 9, 1981

Accepted February 13, 1981